

Fabrication of block copolymer templates by using dually responsive photoresist bottom layers



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ARTICLE INFO

Keywords:

Block copolymer lithography
Dually responsive photoresist
Bilayer system
Nanotemplate

ABSTRACT

A simple and novel method was developed to fabricate a nanoporous template by using a bilayer system composed of a silicon-containing block copolymer top layer and a dually responsive photoresist bottom layer. The dually responsive bottom layer became cross-linked by heating. The cross-linked polymer was mechanically hard and insoluble in common solvents. The block copolymer pattern was transferred to the bottom layer by oxygen reactive ion etching. High-aspect-ratio nanopore arrays were generated. The cross-linked bottom layer became soluble again by chain scission upon exposure to UV light. Therefore, the template with a highly orientated array of cylindrical nanopores could be easily removed by dipping in an aqueous base solution. This versatile template of nanoporous structures could be used to create freestanding 1D nanostructures of a variety of functional materials.

1. Introduction

Arrays of nanostructures such as nanodots, nanorods, nanowires, and nanotubes have been drawing intense research interest because of their potential applications in sensors [1,2] and optoelectrical [3,4], optical [5], magnetic [6], electronic [7], and energy storage devices [8]. One of the major issues of the fabrication of nanostructured arrays is to obtain structures with uniform shape and size over a wide area. Among various methods for the production of nanostructure arrays, template-based approaches have been used extensively [9–11]. Template-based approaches have the advantages of low cost, versatility, and convenience for a large area processing. Both anodic aluminum oxide (AAO) and block copolymer thin films serve well as suitable templates for growing 1-dimensional (1D) nanostructures. The AAO template is usually prepared by a controlled anodization process from an aluminum sheet [12]. The AAO template contains nanopores or nanochannels with high pore density and offers excellent thermal and mechanical stabilities.

The use of block copolymers as templates for the fabrication of nanostructured materials has also elicited much attention [13–22]. The block copolymer, consisting of chemically different polymers, which are covalently connected, assembles spontaneously into various ordered nanostructures, including lamellae, cylinders, and spheres. Furthermore, the morphology and domain size can be tailored by controlling the block ratio and molecular weight of block copolymers. Many researchers have reported the fabrication of nanostructured polymers

[23], metals [24], and semiconductors [25] by using block copolymer templates. However, it remains a challenge to make high-aspect-ratio nanoporous templates over a wide area by using block copolymer thin films. Several methods have been suggested for the preparation of high-aspect-ratio block copolymer nanotemplates with controlled micro-domain orientation.

Our group previously reported a novel method for fabricating a high-aspect-ratio nanoporous template by using a silicon-containing block copolymer top layer and a SU-8 bottom layer [26,27]. However, harsh processing conditions such as dry etch or calcination are required to remove the cross-linked SU-8 template. Therefore, SU-8 is not an appropriate material to fabricate organic nanostructure.

In the present study, we developed a new bottom layer, which could be removed easily. A dually responsive photoresist was introduced as a bottom layer to fabricate a universal nanotemplate. The dually responsive polymer became cross-linked by the thermal treatment and could be used as a hard template during the etching process. It was soluble again by chain scission upon exposure to UV light. Therefore, the template could be easily removed by dipping in an aqueous base solution. As a result, we successfully obtained vertically aligned and highly ordered gold and polypyrrole nanostructures by using the dually responsive nanoporous template. In particular, the template is applicable on various substrates because of the compatibility of the dually responsive photoresist with a wide range of substrates. This versatile template could be used to prepare freestanding 1D nanostructures of functional materials.

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2. Experimental

2.1. Materials

2-(2-Diazo-3-oxo-butyryloxy)-ethyl methacrylate (DOBEMA) and 4-hydroxy-2-methylbutan-2-yl methacrylate (HMBMA) were synthesized according to previously reported procedures [28,29]. Asymmetric polystyrene-block-poly(4-(*tert*-butyldimethylsilyl) oxystyrene) (PS-*b*-PSSi) was prepared by living anionic polymerization according to a reported procedure [30]. The number average molecular weight and polydispersity index were $71,800 \text{ g mol}^{-1}$ and 1.14, respectively, for PS_{22.1k}-*b*-PSSi_{49.7k} ($22,100 \text{ g mol}^{-1}$ for PS and $49,700 \text{ g mol}^{-1}$ for PSSi). Tetrahydrofuran (THF) was purchased from Junsei Chemical Company and distilled from sodium/benzophenone before use. The initiator, 2,2'-azobisisobutyronitrile (AIBN), supplied by Junsei Chemical Company, was purified by recrystallization from methanol. Other chemicals were purchased from Sigma-Aldrich and were used as received.

2.2. Measurements

Chemical structures were determined by ^1H and ^{13}C NMR spectroscopy (Bruker AM-300 FT-NMR-spectrometer and Bruker Avance 400) and IR spectroscopy (Bio-Rad FTS-165 FT-IR spectrometer). The number average molecular weight and molecular weight distribution were determined in THF by a Waters GPC-150C calibrated with polystyrene standards. UV light irradiation was performed using a deep UV exposure system (Oriol Corporation, model 82531) with a filter transmitting light between 220 and 260 nm. Differential scanning calorimetry was performed using TA instruments Auto Q20 system (New Castle, DE) equipped with a refrigerated cooling system (RCS 40) at a heating rate of $10 \text{ }^\circ\text{C/min}$ under N_2 . Film thicknesses were measured using a Tencor Alpha-Step 500 profiler. Thin film thicknesses were determined using a Gaertner L116s ellipsometer (Gaertner Scientific Corp.) equipped with a He-Ne laser (632.8 nm) at a 70° angle of incidence. Atomic force microscopy (AFM) images were obtained using a Nanoscope IIIa multimode scanning probe microscope (Veeco) in tapping mode. Scanning electron microscope (SEM) images were obtained using a Hitachi model S-2280N SEM. The electrodeposition of gold and polypyrrole was performed using an Autolab/PG-STAT12 model system with a three-electrode cell.

2.3. Synthesis of 4-[(*tert*-butoxycarbonyl)oxy]styrene

4-[(*tert*-Butoxycarbonyl)oxy]styrene (t-BOCSt) was synthesized according to a similar method in the literature [31]. 4-Hydroxy styrene (4.7 g, 39 mmol) was added to a solution of 4-dimethylaminopyridine (0.7 g, 5.7 mmol) in dry THF (200 mL). After 5 min, di-*tert*-butyl dicarbonate (8.5 g, 39 mmol) was added. After 20 h of stirring at room temperature, the reaction was quenched with H_2O , and the mixture was extracted with CH_2Cl_2 . After the evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography to afford tBOCSt (3.66 g, 43%) as colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.70 (d, 2H), 7.24 (d, 2H), 6.63 (q, 1H), 5.61 (d, 1H), 5.18 (d, 1H), 1.38 (s, 9H); ^{13}C NMR (400 MHz, CDCl_3) 151.8,

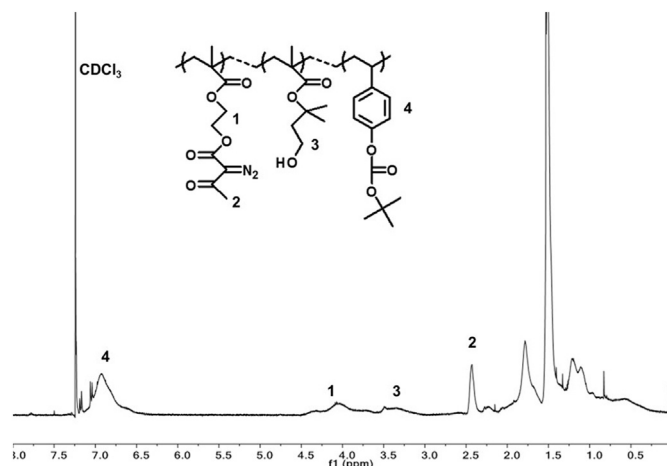
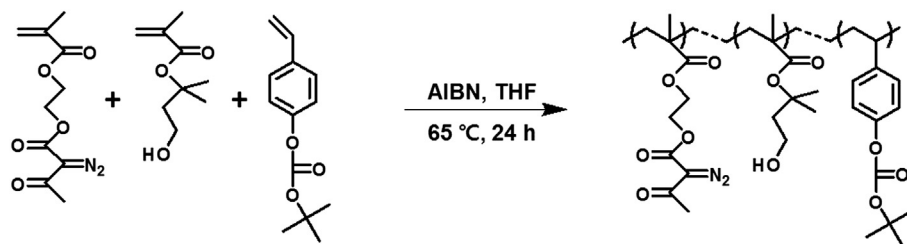


Fig. 2. ^1H NMR spectrum of poly(DOBEMA-co-HMBMA-co-tBOCSt) in CDCl_3 .

149.1, 134.7, 132.8, 127.9, 120.7, 112.9, 82.8, 27.7.

2.4. Synthesis of the dually responsive photoresist

Poly(DOBEMA-co-HMBMA-co-tBOCSt) was prepared by free radical polymerization in a sealed ampoule. DOBEMA (0.48 g, 2 mmol), HMBMA (0.345 g, 2 mmol), t-BOCSt (1.32 g, 6 mmol), and 2.5–7 mol% of AIBN were dissolved in 7 mL THF, and the resulting mixture was heated at $65 \text{ }^\circ\text{C}$ for 24 h. After polymerization, the solution was diluted with THF and precipitated into petroleum ether. The precipitated polymers were collected by filtration and washed with petroleum ether. After drying under vacuum for 24 h, white solids were obtained.

2.5. Preparation of nanoporous templates

A 10 wt% solution of poly(DOBEMA-co-HMBMA-co-tBOCSt) with 5 mol% triphenylsulfonium triflate in cyclopentanone was spin-coated at 1500 rpm for 60 s on a substrate. Triphenylsulfonium triflate was added as a photoacid generator. The film was soft-baked at $90 \text{ }^\circ\text{C}$ for 60 s and cross-linked at $130 \text{ }^\circ\text{C}$ for 15 min. A 1.5 wt% solution of PS-*b*-PSSi in xylene was spin-coated at 3000 rpm for 60 s over the cross-linked poly(DOBEMA-co-HMBMA-co-tBOCSt) film. Solvent annealing of the sample was carried out in a mixed solvent vapor of heptane and toluene with a volume fraction of $V_{\text{hep}}/V_{\text{tol}} = 4$ for 4 h. The pattern of the self-assembled PS-*b*-PSSi thin film was transferred to the bottom layer by oxygen reactive ion etching (RIE) for 25 s (VSRIE-600T; Vacuum Science). The oxygen pressure was 6 mTorr with a flow rate of 30 sccm, a radio-frequency power of 300 W, and a platen power of 50 W.

2.6. Fabrication of polypyrrole nanodot arrays and gold nanorod arrays

Polypyrrole was polymerized electrochemically on the nanoporous template with pores of 50 nm diameter and 155 nm thickness on a gold substrate. Electrodeposition was performed using a three-electrode system with a working electrode of gold, a counter electrode of

Fig. 1. Synthesis of poly(DOBEMA-co-HMBMA-co-tBOCSt).

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